Chemical components of bleached eucalypt kraft pulp effluent COD and treatment removal efficiency during normal mill operation and maintenance shutdowns

C. L. S. Rodrigues, A. H. Mounteer, T. V. Stoppa and L. C. Dalvi

ABSTRACT

In order to meet increasingly strict Brazilian COD emissions limits, mills must understand the components that contribute to effluent COD, how these vary between normal mill operation and maintenance shutdowns, and how this variation affects treatment efficiency. To this end, primary and secondary effluents from a Brazilian bleached eucalypt kraft pulp mill activated sludge system were analyzed for COD, lignin, extractives, carbohydrates and AOX over a sixth month period that included two general maintenance shutdowns and four months of normal operation. Primary effluent presented significantly different compositions during periods of normal operation and mill shutdowns. During normal operation, the main components of effluent COD (909 mg/l average) were carbohydrates, followed by lignin. However, the lignin fraction was the main component of secondary effluent COD during both normal operation and mill shutdowns. Higher removal efficiencies for COD carbohydrates and AOX were observed during normal operation compared to shutdowns, while no difference in removal efficiencies of lignin and extractives was observed. Carbohydrate removal efficiency was significantly lower in one of the parallel treatment lines. The different removal efficiencies reflect not only variations in effluent composition, but possibly differences in system operational control which should be explored in greater detail

Key words | activated sludge, AOX, carbohydrates, COD, eucalypt, extractives, lignin

C. L. S. Rodrigues
A. H. Mounteer (corresponding author)
T. V. Stoppa
Civil Engineering Department,
Federal University of Viçosa,
Viçosa, MG,
Brazil
E-mail: *cleuber@gmail.com*;
ann@ufv.br;
teynha.stoppa@ufv.br

L. C. Dalvi
Celulose Nipo-Brasileira,
Belo Oriente, MG,
Brazil
E-mail: *leandro.dalvi@cenibra.com.br*

INTRODUCTION

Brazil is the largest producer and exporter of bleached eucalypt kraft market pulp in the world (Bracelpa 2009). The pulp and paper industry is considered the sixth largest source of environmental pollution worldwide, behind the oil, cement, leather, textile and steel industries (Ali & Sreekrishnan 2001). Water pollution is one of the largest concerns in the pulp and paper industry because mills produce large volumes of effluents with high organic loads that are partly recalcitrant and potentially toxic. Until the 1980s the principal concern with regard to release of effluents containing high organic loads was due to depletion of oxygen and effluent treatment systems and receiving water quality were monitored principally with regard to biochemical oxygen demand (BOD) and suspended solids (SS). However, with the implementation of better process control and wastewater treatment systems, concern has shifted to the recalcitrant organic compounds, included in the chemical oxygen demand (COD) not removed during conventional treatment.

Effluent treatment in bleached kraft pulp mills is performed almost exclusively in aerobic biological systems such as activated sludge and aerated lagoons because of the presence of potential inhibitors of anaerobic processes, such as sulphate. These systems are able to reduce BOD by 85–95% but COD by only 40–80% because of the presence of recalcitrant organic compounds (Mounteer *et al.* 2007).

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Furthermore, effluent quality and treatment efficiency can be expected to vary during normal mill operations and mill maintenance shutdowns.

Celulose Nipo-Brasileira (Cenibra), located in Belo Oriente, Minas Gerais, Brazil, produces approximately 1.15 million tons per year of bleached eucalypt kraft market pulp. Pulp is produced in two fibre lines (L1 and L2), using isothermal cooking, oxygen-delignification and a $D_{HT}E_{OP}DP$ ECF bleaching sequence (D_{HT} = hot chlorine dioxide stage; Eop = oxygen and hydrogen peroxide reinforced extraction stage; D = chlorine dioxide stage; P = final hydrogen peroxide stage). Specific water consumption is about 30 m^3 per ton of bleached pulp. Use of the D_{HT} stage has become conventional practice in Brazilian eucalypt kraft pulp mills and was fully implemented at Cenibra in 2007. It has been shown in the laboratory that use of the D_{HT} stage is beneficial in reducing effluent AOX, but is detrimental to effluent biodegradability (Gomes *et al.* 2007). However, the authors have found no reports in the literature on effluent quality and treatment efficiency after implementation of the D_{HT} stage at the industrial level.

Effluent treatment at the Cenibra mill is performed separately for high organic load (from pulping, bleaching and evaporation) and low organic load (from debarking, chemical plant and pulp dryers) effluents. The high organic load effluents from the two fibre lines (HL1 and HL2) pass through separate screens and grit chambers and are then mixed and neutralized at the entrance of the effluent treatment plant. The mixed HL effluent flow is split and treated in parallel primary clarifiers followed by passage through cooling towers where effluent temperature is reduced to 35°C. The HL effluent (3,000 m^3/h) then enters parallel activated sludge systems (S1 and S2). Each system is composed of an aeration tank (nominal 10 hour hydraulic retention time and 20 day mean cell residence time) followed by two secondary clarifiers. The secondary effluent is discharged to the Doce River after mixing with the clarified low organic load effluent. Mill COD discharge limits of 15 kg per air dried tonne of pulp (kg/adt) were established in 2008.

The Cenibra mill performs regularly scheduled mill maintenance shutdowns every six months, in which each fibre line is shut down individually and residual liquors, filtrates, etc. are sewered to the wastewater treatment plant while the other fibre line operates normally. Monitoring of the mill HL effluent treatment plant has shown that both primary and secondary effluent COD can vary considerably during normal mill operation and general mill maintenance shutdowns (Figure 1). Although effluents have not exceeded COD limits, COD discharge during normal mill operation can vary from 4.5 kg COD/adt of pulp (1,100 kg COD/d) to 10 kg COD/adt of pulp (2,340 kg COD/d) as shown by the variation in treated effluent quality in Figure 1. Mill personal are therefore interested in understanding the nature of effluent COD and the factors that affect COD removal efficiency in the effluent treatment plant, since they have observed changes in treatment efficiency after the implementation of the D_{HT} stage in both bleaching lines.

The objective of this study was thus to characterize the chemical nature of COD in primary and biologically treated effluents and to evaluate COD removal/treatment efficiency in the parallel activated sludge treatment systems during normal mill operation and mill maintenance shutdowns. It is hoped that the results will lead to insights on how to improve treatment system operation at the mill.

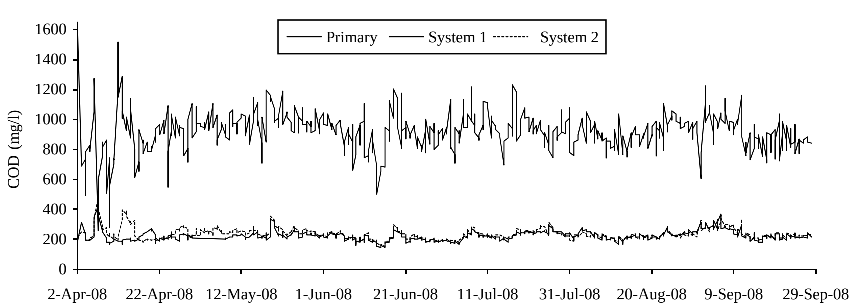

Figure 1 | COD profiles of primary (upper trace) and biologically treated effluent during a six-month monitoring period, including two maintenance shutdowns (in April and September). (Systems 1 and 2 refer to treated effluents from the parallel treatment systems).

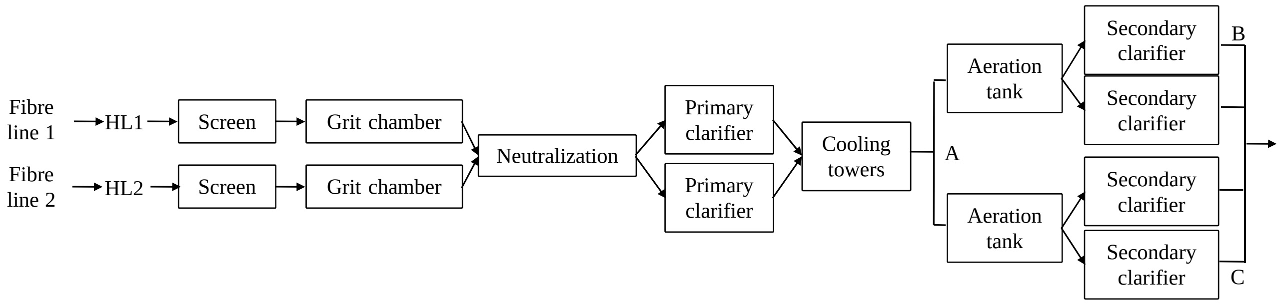

Figure 2 | Flow diagram of high organic load effluent treatment at the mill, indicating locations of effluent sampling points. (A-primary effluent; B-treated effluent, system 1; C-treated effluent, system 2).

METHODS

Effluents

Figure 2 presents a flow diagram of the HL effluent treatment system with sample collection points identified. Effluents were collected at the entrance to the aeration tanks and overflow of the secondary clarifiers. Ten litre grab samples were collected once a month and shipped to the Federal University of Viçosa's Water Quality Control Laboratory (WQCL), where they were stored frozen, under a nitrogen atmosphere until analyzed. Table 1 presents the mill operating conditions on each of the sample collection dates.

Analytical procedures

Effluents were filtered (AP40, Millipore, Billerica, USA) and then characterized by quantifying sum parameters (COD, AOX, lignin, carbohydrates and extractives). AOX, COD and lignin were quantified using the procedures detailed in the Standard Methods (1998). AOX was quantified in an automated analyzer (Euroglas, Delft, Holland). COD was quantified by the closed reflux, colorimetric method. Lignin was quantified after removal of extractives in dichloromethane, and reaction with Folin-phenol reagent. Extractives in dichloromethane were analyzed by a gravimetric method (Silvestre *et al.* 2005). Carbohydrates were quantified colorimetrically (488 nm) after reaction with phenol in acid medium (10 min, 30°C), using the method proposed by Dubois *et al.* (1956). AOX and extractives analyses were performed in duplicate at the mill and COD, lignin and carbohydrates were analysed in triplicate at the WQCL.

COD conversion factors (Table 2) proposed by Basta *et al.* (1996) for eucalypt ECF bleaching effluents were used to convert extractives, lignin and carbohydrates to COD. This conversion was done to evaluate the applicability of the factors to modern eucalypt kraft pulp mill effluents containing D_{HT} bleaching stage filtrates.

Table 1 | Mill operating conditions and effluent composition on sample collection dates

Date	Mill operation	Effluent
04/02/08	Shutdown	HL1 & Line 2 drainage
04/07/08	Shutdown	Line 1 drainage & HL2
05/08/08	Normal	HL1 & HL2
06/12/08	Normal	HL1 & HL2
07/17/08	Normal	HL1 & HL2
08/05/08	Normal	HL1 & HL2
09/23/08	Shutdown	Line 1 drainage & HL2
09/27/08	Shutdown	HL1 & Line 2 drainage

Statistical analysis

Primary and secondary effluent quality during normal operation and mill shutdowns was compared by analysis of variance, followed by comparison of means ($\alpha = 0.05$, two-tailed) of the sample chemical characteristics on each sampling date. Comparisons of effluent quality and treatment efficiency were made between normal operation and mill shutdowns and between activated sludge systems 1 and 2.

RESULTS AND DISCUSSION

COD values of the primary and biologically treated effluent samples are presented in Figure 3. It is readily apparent

Table 2 | Factors used to convert chemical components to COD (Basta *et al.* 1996)

Component	Conversion factor
Carbohydrates	1.2
Extractives	2.7
Lignin	1.9

from the histograms that less than half of the effluent soluble COD was accounted for in the carbohydrate, extractives and lignin fractions, when using the conversion factors in Table 2. We do not believe that such a large fraction of soluble COD belongs to chemical classes other than lignin, carbohydrates and extractives, but rather that the conversion factors used are not appropriate for modern eucalypt bleached kraft mill effluent. These factors were derived as general conversion factors for both softwood and hardwood effluents in the 1990s, before the wide scale implementation of the D_{HT} bleaching stage, which has been shown to significantly impact effluent treatability and COD recalcitrance in eucalypt bleaching effluents (Gomes *et al.* 2007; Mounteer *et al.* 2007). In the work by Basta *et al.* (1996), COD in untreated effluent from oxygen delignified eucalypt bleached kraft pulp prepared in the laboratory could be assigned to carbohydrates (40%), lignin (20%), extractives (10%), methanol (10%) and organic acids (<2%), while 20% was left unaccounted for using the conversion factors the authors proposed. No results were reported on COD composition after laboratory-scale biological treatment of the oxygen-delignified eucalypt bleached kraft pulp effluent, but the authors noted that final effluent contained no methanol or organic acids and only small proportions of carbohydrates and extractives.

The analytical methods used to characterize the effluents may have contributed in part to the low proportion of soluble COD quantified after conversion of the different

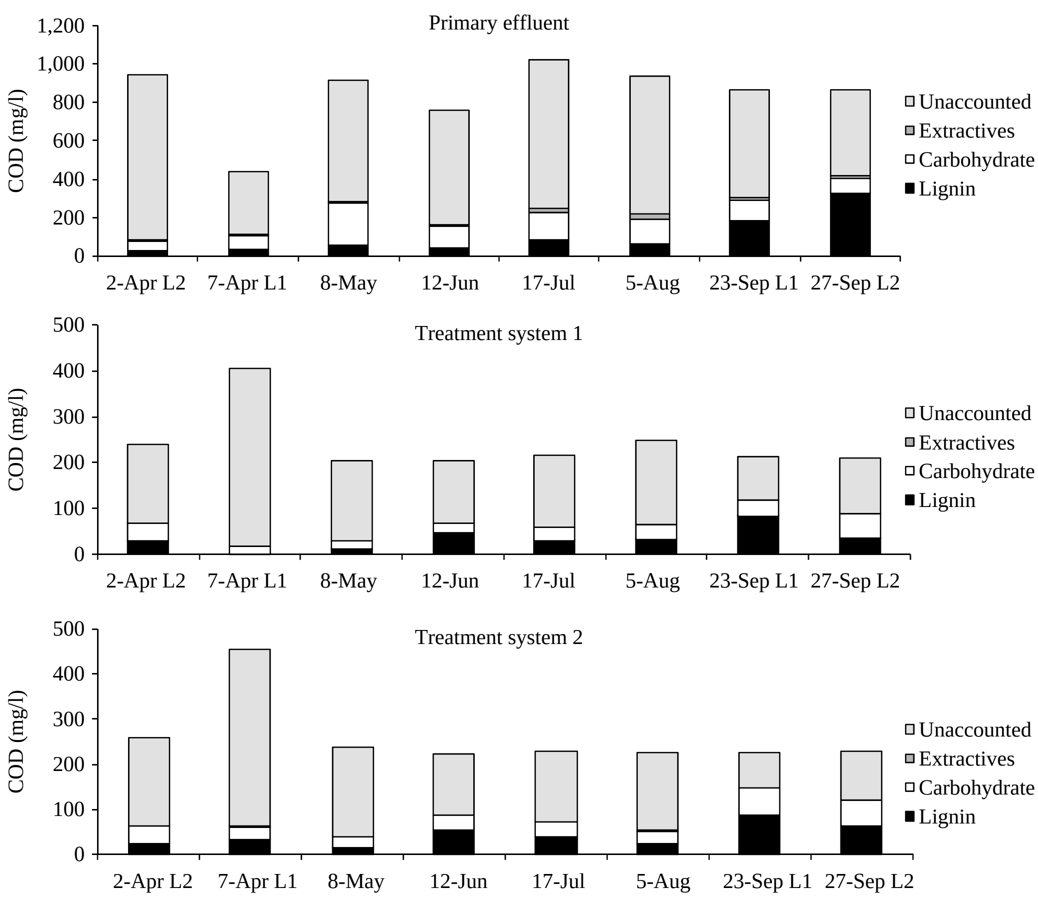

Figure 3 | Chemical oxygen demand (COD) components in primary and biologically treated bleached kraft pulp effluent in activated sludge treatment systems 1 and 2 during normal mill operation and mill maintenance shutdowns. (L1 or L2 after the sample date indicates which fibre line was under maintenance shutdown during sampling).

components to COD equivalents. Lignin was quantified using the Folin-phenol method that quantifies all aromatic hydroxyl groups that react with the reagent (APHA 1998). Therefore, partially degraded residual lignin, without intact aromatic rings was not quantified. Furthermore, very low extractives contents were found using the gravimetric method employed at the mill and these values will be confirmed by using another quantification method (Silvério *et al.* 2006). The main classes of lipophilic extractives in eucalypt bleached kraft mill effluents are fatty acids and phytosterols, while resin acids are not encountered (Gutiérrez *et al.* 2001). Phytosterols are of particular interest since they have been implicated in adverse environmental effects of biologically treated pulp mill effluents (Kostamo *et al.* 2004). However, the phytosterols most commonly found in eucalypt bleached kraft pulp mill effluents (β-sitosterol, campesterol and stigmasterol) are generally adsorbed on suspended solids and leave the systems through excess sludge wasting (Nieminen *et al.* 2002; Kostamo & Kukkonen 2003). Furthermore, it has previously been shown that over 90% of the soluble COD in the secondary effluents from the mill evaluated in the present study are found in substances with molar mass greater than 500 g/mol (Morais *et al.* 2008), precluding significant contributions from fatty acids and phytosterols to this COD. Therefore, we believe that the conversion factors developed for more conventional ECF softwood and hardwood kraft pulp effluents are no longer valid and new conversion factors for the major COD chemical classes in modern eucalypt bleached kraft pulp mill effluents should be developed to account for a greater proportion of the COD.

Soluble COD in primary effluent varied considerably during both normal operation and mill maintenance shutdowns. The lowest COD was observed on April 7, when fibre line 1 was shutdown for maintenance. However, this result was not repeated on the second shutdown of fibre line 1 (Sept. 23). The mill did not report significant differences in maintenance operations during these periods that would account for these differences.

The lignin component of the chemically characterized COD showed the greatest variability in the primary effluent and its contribution to the effluent COD generally increased after secondary treatment, as reported previously (Morais *et al.* 2008). The proportion of carbohydrates in primary effluent was higher during normal operation than during maintenance shutdowns. However, no clear trend was observed with regard to COD chemical components in treated effluents during normal operation and mill maintenance shutdowns. Interestingly, the primary effluent with the lowest COD (April 7) resulted in the treated effluent with the highest COD, almost all of it in the uncharacterized fraction. Although the proportions of the chemically characterized and uncharacterized fractions of treated effluent COD were similar in systems 1 and 2, final COD from treatment system 1 showed less variability than from treatment system 2 on the dates sampled. This is an indication of different treatment efficiencies in the parallel treatment plants, since they both receive the same effluent, during both normal operation and mill shutdowns (Figure 2).

Comparison of primary effluent quality during normal operation and maintenance shutdowns (Table 3) showed that, whereas COD values were not significantly different, carbohydrate and AOX values were higher during normal operation and lignin values were higher during shutdowns. The lack of significant differences in primary effluent COD stems from the large daily variations in COD values, as previously mentioned (Figure 1). Higher carbohydrate and AOX values during normal operation are evidence of the contribution of fibre line bleaching effluents to HL1 and HL2 effluents. The greater amount of lignin during mill maintenance shutdowns probably reflects contributions from the pulping and recovery systems, which contain aromatic hydroxyl groups, potentially quantified in the Folin-phenol reaction (Standard Methods 1998).

Treatment efficiencies during normal operation and maintenance shutdowns in the parallel activated sludge

Table 3 | Comparison of primary effluent quality during normal operation and maintenance shutdowns*

	Operation	
Characteristic	**Normal**	**Shutdown**
COD (mg/l)	909 a	778 a
Carbohydrates (mg/l)	128 a	63 b
Lignin (mg/l)	32 b	76 a
AOX (mg/l)	6.4 a	3.7 b

*For each characteristic, values followed by the same letter are not significantly different ($p = 5\%$).

Table 4 | Removal efficiencies (%) in parallel activated sludge systems (S1 and S2) during normal mill operation and mill maintenance shutdowns (average values ± one standard deviation, $n = 8$ to 12)

Parameter	System	Normal	Shutdown
COD	S1	75 ± 2.4	57 ± 34.1
	S2	74 ± 2.4	55 ± 38.8
Carbohydrates	S1	83 ± 6.4	48 ± 28.8
	S2	80 ± 7.4	36 ± 19.4
Lignin	S1	63 ± 16.5	61 ± 43.2
	S2	40 ± 44.7	41 ± 31.7
AOX	S1	55 ± 2.7	34 ± 23.1
	S2	53 ± 5.6	32 ± 19.1
Extractives	S1	92 ± 10.4	100
	S2	92 ± 12.2	99 ± 1.5

systems (S1 and S2) are compared in Table 4. Removal efficiencies for COD, carbohydrates and AOX were lower during maintenance shutdowns than during normal operations, whereas removal efficiencies for lignin and extractives were apparently unchanged. The lower overall COD removal efficiency during maintenance shutdowns may be in part due to the altered COD composition (Figure 3) that affected its biodegradability. The lignin component, which increased during maintenance shutdowns, and is considered to contribute to the recalcitrant COD in bleached pulp mill effluents (Hewitt *et al.* 2006), was removed with equivalent efficiencies during normal operation and maintenance shutdowns. Lower carbohydrate removal efficiencies were observed during maintenance shutdowns, which is probably a reflection of the lower carbohydrate concentration in the primary effluent during these periods (Table 3). The lower AOX removal efficiency during maintenance shutdowns also probably reflects the very low AOX values in the primary effluent during these periods (Table 3).

The different treatment efficiencies are confirmed by the results in Table 5, which show that both activated sludge systems produced significantly lower final COD and carbohydrates and higher AOX during normal operation than during maintenance shutdowns. Final effluent lignin levels were lower during normal operation only in system 2.

Comparison of activated sludge systems 1 and 2 showed no significant differences in effluent quality during normal operation but significantly higher values of COD, carbohydrates and lignin in effluents from system 2 than from system 1 during mill shutdowns (Table 5). Since the two activated sludge systems receive virtually the same effluent (Figure 2), and operate at the same hydraulic retention times and sludge ages, the different final effluent qualities may reflect control differences. The main differences in operational control between the parallel activated sludge systems are related to aeration intensity, nutrient and antifoaming agent dosages that vary on a day-to-day basis, due to unforeseen equipment failures (dosing pumps, aerators, etc.).

Table 5 | Comparison of effluent quality in activated sludge systems 1 and 2 during normal operation and maintenance shutdowns* (values are averages of 8 to 12 analyses)

Characteristic	Treatment system	Operation Normal	Shutdown
COD (mg/l)	S1	218 b, A	267 a, B
	S2	229 b, A	292 a, A
Carbohydrates (mg/l)	S1	21 b, A	30 a, B
	S2	24 b, A	39 a, A
Lignin (mg/l)	S1	16 a, A	20 a, B
	S2	18 b, A	27 a, A
AOX (mg/l)	S1	2.9 a, A	2.4 b, A
	S2	3.0 a, A	2.5 b, A

*In each line, values followed by the same lower case letter are not significantly different ($p = 5\%$). In each column, for each effluent characteristic, values followed by the same upper case letter are not significantly different ($p = 5\%$).

CONCLUSIONS

COD removal efficiency in a eucalypt bleached kraft pulp mill activated sludge treatment plant was higher during normal operation than during maintenance shutdowns, indicating a negative impact of black liquor and evaporator condensates sewered to the treatment system during mill shutdowns on effluent treatability. While the parallel activated sludge systems operated at the same hydraulic and sludge retention times presented equal treatment efficiencies during normal operation, the systems presented different COD, lignin and carbohydrate removal efficiencies during maintenance shutdowns. These findings suggest that day-to-day operational control of the activated sludge systems have a significant impact on treatment efficiency, especially during maintenance shutdowns. Future studies should be undertaken to investigate the relationships between effluent variability, treatment system operational control and treatment efficiency. Conversion factors for the main chemical components of modern ECF bleaching effluent COD should also be estimated for use in COD treatability studies and the impacts of mill operating conditions on effluent quality.

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